THE RELATIONSHIP BETWEEN CHAR REACTIVITY AND PHYSICAL AND CHEMICAL STRUCTURAL FEATURES

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INTRODUCTION

This study focuses on correlations observed between char reactivity, on the one hand, and char resistivity and structural properties on the other. It is the continuation of a study reported recently on the relationship between char reactivity and pyrolysis conditions (1). There, it was found, as others have observed before (2-5), that for most coals, reactivity decreases with increasing degree of pyrolysis. As pyrolysis progresses a number of changes occur in the char: hydrogen and oxygen content decrease, a greater degree of order is brought about and changes occur in the sample shape, pore size distribution and surface area.

With so many factors varying, the observation of a correlation between char reactivity and one factor need not imply a cause and effect relationship between the two. The traditional way to deduce cause-and-effect is to vary only one factor at a time, and observe its effect on the measurement. This is not readily done for chars. The result is that the research in char reactivity has established trends, but not a quantitative theory.

A great deal is known about char reactivity, as can be seen from two reviews of the subject (4,5). For the present work, only a subset of this information is needed, which we take from the reviews. Correlation of char reactivity has been made with heteroatom content (oxygen and hydrogen in this instance), with structure and with mineral content. The "structure" generally refers to the number of exposed edge atoms of lamellae (6,7). In pure graphite these sites have been shown to be the most reactive towards oxidation, and it is commonly held that these edge sites are most reactive in chars, also. An exception to this is the location of sites activated by mineral matter. These sites are found in the basal plane of graphite (4). Reactivities have also been correlated with resistivity (8).

In this work, chars have been characterized with respect to reactivity, surface area, heteroatom content, ash content, x-ray diffraction, and resistivity. The char characteristics have been correlated with coal rank, coal mineral content, and the heating rate and final temperature used for char preparations. The paper presents a summary of the observed trends.

EXPERIMENTS

Char Preparation

The experiments described here were carried out on a char formed from phenol formaldehyde resin, as described by Suuberg, et al. (9) and on chars formed from raw and demineralized coals and lignites. Demineralization was carried out by the procedure of Bishop and Ward (10). The chars were formed by heating in an inert gas within an entrained flow reactor (EFR) for a variety of residence times and maximum temperatures, or by heating in a Thermogravimetric Analyzer (TGA) at 30°C/min to 600, 700, 800 or 900°C. The composition of the starting material as well as those of the charred materials, are shown in Table I.

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Reactivity Measurements

Initial char reactivity measurements were made using the isothermal technique developed at Pennsylvania State University (11). In this method, the char is heated in a TGA in nitrogen to the desired temperature, usually 400-500°C. The time for 50% burnoff, $\tau_{0.5}$, is used as the reactivity index. In our char characterization work, we had difficulty applying the isothermal techniques to chars formed over a wide range of conditions. A temperature level selected for one char was inappropriate for another.

In order to overcome this difficulty, a non-isothermal technique was developed using a Perkin-Elmer TGA 2 (1). The sample (about 1.5 mg) is heated in air at a rate of 30 K/min until a temperature of 900°C is reached. The TGA records the sample weight continuously and, at the end of the experiment, the weight and derivative are plotted. The temperature (T_{cr}) at which the derivative of the fractional weight loss with respect to time reaches a value of 0.11 wt. fraction/min was chosen as an index of reactivity. This was compared with the $\tau_{0.5}$ values measured by the isothermal technique and a good correlation was observed (1).

Surface Area Determinations

The surface areas reported in this paper have been obtained at Brown University using a Quantasorb instrument, manufactured by Quantachrome, Inc. The sample cell is immersed in liquid N_2 for N_2 adsorption or a dry ice-acetone bath at -78°C, for CO_2 adsorption. Determinations of surface area from the sorption data have been made using classical BET theory; typically three points have been taken at values of (P/P_o) of 0.1, 0.2, and 0.3.

X-Ray Diffraction Measurement

Powder diffraction patterns were recorded on film with a Debye-Scherrer camera (dia. 57.3 mm), in air. The films were read with a diode-phototransitor pair, feeding a logarithmic amplifier whose output drove the Y-channel of an X-Y recorder. The X-Y chart record, then, is of film darkening (proportional to x-ray intensity) versus distance along the film. Graphite was the reference material. The sample capillary diameter (0.5 mm) and the aperture of the limiting slit in the film reader, were chosen so that the **(100)** and **(101)** lines of graphite were resolved.

Where intensity measurements of more than one sample are compared, the same exposure conditions and times were used to record the data. The background scattering from air and capillary were determined by a "blank" (empty capillary) run, and sample densities were estimated from the sample contribution to the large angle scattering, assumed to be incoherent (12). Heteroatom contribution was not taken into account when estimating the sample density. "Line" intensities were determined by subtracting the interpolated smooth background from the corrected data.

Resistivity Measurements

The apparatus that was used for the sample cell in the electrical resistivity tests is similar in form to that described by Mutso and DuBroff (8), although smaller. In the apparatus used here, a small amount of sample (about 15 mg) is introduced into the cell, and the electrical resistance of the sample, under a constant pressure of 1000 p.s.i. is measured by a digital ohm-meter. Both the exact ($\pm$ 0.1 mg) sample weight and compressed density are determined, and from these measurements and the known cell dimensions, a resistivity is calculated.

It is possible that interparticle resistance, as well as the intrinsic material property, contributed significantly to the measured resistivity. This possibility was investigated for a number of chars by measuring the resistivity for a sieved sample (-200 +325 mesh), and a sample ground to micrometer sized particles. A small effect was seen, although all measurements on one char were within $\pm$ 5%.

Likewise, the effect of char drying on resistivity was investigated. No significant effect was observed between the resistivity of chars that had been in jars for several days, and that of freshly dried material.

RESULTS AND DISCUSSION

Reactivity vs. Extent of Pyrolysis

Figure 1 summarizes the results for chars from the five coals. This figure is based on Fig. 5 of Ref. 1 with additional coals and with measured values rather than calculated values of hydrogen for the Kentucky No. 9 chars. The critical temperature (T_{cr}), which varies inversely with reactivity, is plotted as a function of the (daf) hydrogen content, which is used as a measure of the extent of pyrolysis. For each char type, there is a trend for increasing T_{cr} (decreasing reactivity) with decreasing hydrogen. Most of the change occurs below 2 1/2% hydrogen, after the evolution of aliphatic hydrogen is complete. That is, T_{cr} appears to vary primarily with the concentration of aromatic hydrogen. This variation could be due to a variation in the active site concentration, possibly correlated with the ring condensation accompanying the elimination of aromatic hydrogen. There does not appear to be any drastic effects due to heating rate for low rank coals containing minerals, as chars for a wide range of conditions all fell along the same curve. The preliminary results for bituminous coals and demineralized low rank coals do not exhibit the same degree of reactor independence.

It should be noted that there is also ring oxygen in the char which is removed at about the same rate as the hydrogen and which may be related to the reactivity changes. Similar correlations were observed with oxygen concentration for chars produced from a single coal, i.e., the reactivity decreases with decreasing char oxygen concentration. However, it is thought that the hydrogen is the major indicator of reactivity, since it is present at about five times the level of oxygen on an atomic basis. Our studies indicate that the oxygen content of the parent coal is more important (see below).

The upper solid line in Fig. 1 is a "best fit" line drawn through the data for Kentucky No. 9 and Pittsburgh Seam bituminous chars. The lower solid line is a best fit line drawn through the Zap lignite chars.

Reactivity vs. Mineral Content

It is known that the vertical displacement of the curves in Fig. 1 is at least partly due to the variations in catalytic activity of minerals. This effect has been observed in previous studies which have been reviewed by Mahajan and Walker (13). The most reactive chars are for the Zap lignite which are known to have a high Na and Ca content. The results for T_{cr} versus daf hydrogen content for Zap chars demineralized by two procedures are shown in Fig. 2. In both procedures, the Bishop and Ward technique (10) was used, except that in procedure 1 the HF was used at one-fifth normal strength. It is apparent that this produced a lower extent of demineralization, which was verified by XPES analysis. Both data sets are compared to the "best fit" line drawn through the Zap data in Fig. 1. It is evident that reactivity results for the Zap demineralized by procedure 2 are similar to chars from bituminous coals (see Fig. 1). Samples of Pittsburgh Seam and Illinois No. 6

bituminous coals were also subjected to demineralization but did not exhibit as dramatic an effect.

Reactivity vs. Surface Area

Another area of investigation was the differences in surface area among the chars that were tested for reactivity. N_2 surface areas varied from 1 to over 100 m^2/gram. In general, for any given coal, N_2 surface areas went up with decreasing hydrogen content below 3% hydrogen, where the reactivity was observed to decrease. N_2 surface areas also increase with the extent of burnoff at essentailly constant reactivity. So reactivities do not correlate with N_2 surface areas.

CO_2 surface areas varied from around 10 to over 300 m^2/gram with almost all chars in the range of 100 to 300 m^2/gram. The CO_2 surface area which varies by factors of 3 shows no correlation with reactivity which varies by factors of 100.

The fact that reactivities do not correlate with surface is not surprising. As discussed by Walker and coworkers (3,7,13), it is the active surface area (ASA) as measured by oxygen chemisorbtion which is important. However, Suuberg, et al., (9) have recently called into question the utility of oxygen chemisorbtion as a technique for measuring the ASA of "young" chars. In this work, we have not attempted to measure ASA's.

Reactivity vs. Rank

A systematic study of the variations of reactivity with coal rank has been performed. Figure 3 presents a correlation between the oxygen content in the parent coal and the reactivity of char produced in the TGA by heating in nitrogen at 30°C/min to 900°C. The open squares are results obtained for raw coals, the solid squares show the results for demineralized coals. For raw coals there is a decrease in reactivity with increasing rank. Similar results were summarized by Mahajan and Walker (13). For demineralized coals above 8% oxygen, the reactivity does not vary with oxygen. The results suggest that the decrease in reactivity with increasing rank is a property of the organic matter at high rank (less than 8% oxygen) and mineral matter at lower rank (greater than 8% oxygen).

Reactivity vs. Molecular Order

For a series of chars formed from Eastern and demineralized Western coals and lignites, the reactivity and the x-ray diffraction patterns were measured. With increasing degree of pyrolysis, T_{cr} increases, indicating reduced reactivity (1). This correlation has been observed before (7). Also with increasing degree of pyrolysis, the extent of ordering increases, as indicated by the greater intensity and lower breadth of the **(10)** diffraction line from the chars (Fig. 4). Franklin was amongst the first to describe this particular correlation (14). Combining the two, it is seen that there is a correlation between decreasing reactivity and increasing order, apparently implicating lamellae edges as the active sites.

In looking for a parameter from the x-ray scattering data to characterize "order" in a simple way, it is noted that most workers in the field use crystallite diameter, L_u. For ideal crystallites, the diameter can be found from the breadth of the **(10)** line, or its angular shift$_o$(15). For the chars investigated in this work, lamellae diameters are under 30 A, and do not change dramatically during pyrolysis. On the other hand, the intensity in the **(10)** band, for a fixed density of lamellae, increases as N^2, where N is the number of atoms in the lamellae (15). Under these circumstances, the intensity increases with L_u to the fourth power. The intensity is a very sensitive measure of lamellae growth, and therefore, of order. This is the parameter which Radovic, et al. used in their work (7).

Figure 5 presents the intensity of the (10) band versus the critical temperature, for a number of chars formed by slow heating. These chars were all prepared from demineralized chars to avoid interference from the mineral diffraction lines. It is seen that there is a trend of increasing intensity of the (10) band with increasing T_{cr}. In other words, the chars become less reactive as they become more ordered (7). As mentioned above, other properties of the char change with increasing heat treatment. It has not been demonstrated here that the correlation in Fig. 5 is one of cause and effect; the relationship is as expected, however (5). Chars created at high heating rates (not shown) appeared to fall near the other chars but with higher uncertainty due to their low density.

Reactivity vs. Resistivity

In continuing to seek correlations between char reactivity and other parameters, we were led by the work of Mutso and DuBroff to investigate the relationship between reactivity and resistivity (8).

In the work described in Ref. 8, and other earlier wqrks, the relationship between reactivity and resistivity was performed for cokes, formed from coking coals which come from a relatively narrow range of coal rank. In the present case we plot reactivity, indicated by T_{cr}, versus resistivity, for a wider range of starting coals, including the demineralized lignite, as well as for the resin char (Fig. 6).

Also in Fig. 6 are plotted data points for chars formed from North Dakota lignite without treatment. These are the points on the line far removed from the shaded band which encompasses all other points. For Eastern coals, and for demineralized Western lignite, there is an excellent correlation between char reactivity and electrical resistivity.

The removal of the data points from the shaded band for lignite with minerals, can be traced to the effect of minerals on reactivity (4). The minerals do not have a major effect on resistivity for the samples measured here.

CONCLUSIONS

Results are presented which are used to make, or to restate, the following conclusions:

- A new test has been developed which allows relative reactivity to be determined for chars of widely varying reactivity.
- Reactivity was found to decrease with increasing extent of pyrolysis, as determined by (daf) hydrogen content.
- The effect of heating rate or reactivity appeared to be unimportant for non-demineralized low rank coals.
- The differences in reactivity of chars do not depend strongly on the char surface area measured by N_2 or CO_2.
- For coals with more than 8% oxygen, mineral effects appear to be important in determining reactivity differences between chars from different coals.
- A relationship between extent of order and char reactivity is demonstrated for chars formed by slow heating. This is done by plotting T_{cr} against the intensity of the (10) x-ray diffraction line.

- The work done by others (8) showing a correlation between coke reactivity and electrical resistivity, is extended to chars. Again, a correlation is observed, although only in the absence of mineral effects.

ACKNOWLEDGEMENT

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TABLE I

Composition of Starting Demineralized Coals and Chars (wt% DAF)

	Carbon	Hydrogen	Nitrogen	Ash
Zap Lignite	63.54	4.32	0.79	0.18
Lignite Charred in EFA to 0"	78.85	2.55	1.05	0.76
8"	86.31	1.36	0.79	0.60
16"	87.55	0.93	0.91	1.54
24"	88.74	0.51	0.53	0.43
Lignite Charred in TGA at 30°C/min to a final temp. of 600°C				0.38
700°C				0.37
800°C				0.49
900°C				0.29
Pocahontas Coal	91.03	4.71	0.98	1.54
Rosebud Coal	72.10	4.90	1.20	3.68
Pittsburgh Seam Coal	80.90	5.50	1.40	2.31

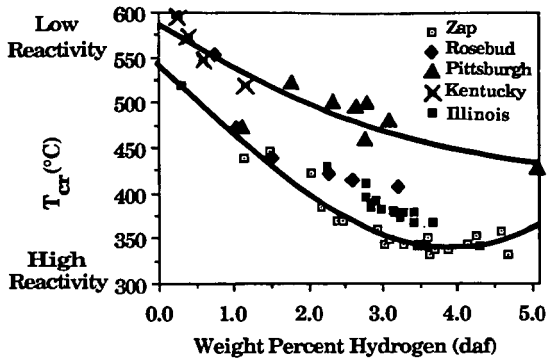

Figure 1. Comparison of Reactivity for Chars from Five Coals of Various Rank as a Function of Hydrogen Concentration. T_{cr} Varies Inversely with Reactivity.

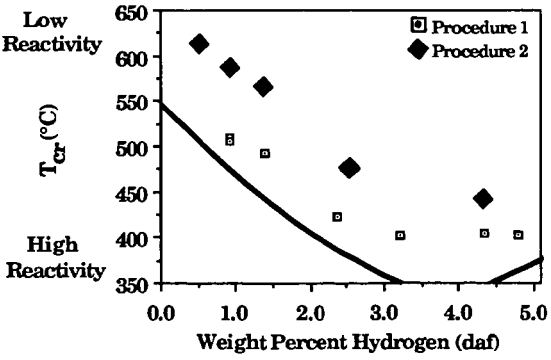

Figure 2. Comparison of Reactivity of Chars from Demineralized Zap Lignite (data) with Chars from Raw Zap Lignite (line from Figure 1). Procedure 1 was a Modification of the Bishop and Ward (ref.10) technique with a Lower HF Strength. Procedure 2 was the Standard Bishop and Ward Technique.

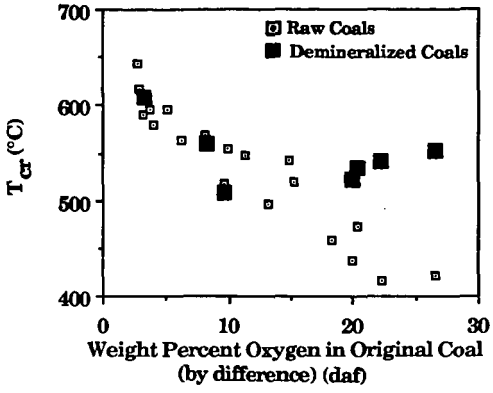

Figure 3. Variation of Reactivity with Coal Oxygen Content for Chars Prepared by Heating in Nitrogen at 30°C/min to 900°C.

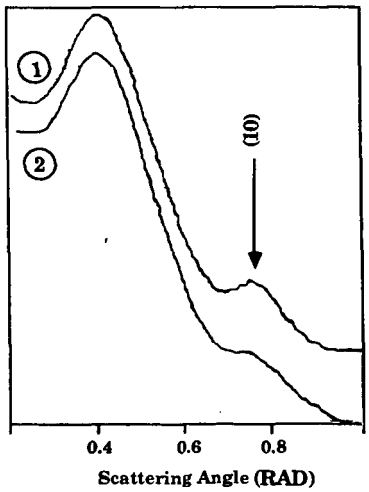

Figure 4. Diffracted X-ray Intensity Versus Angle, for Two Chars Formed from Demineralized North Dakota (Zap) Lignite. The Curves have been Displaced Vertically to Facilitate Comparison. The Char for (1) was Formed by Heating at 0.5°C/sec to 900°C; for (2) to 600°C.

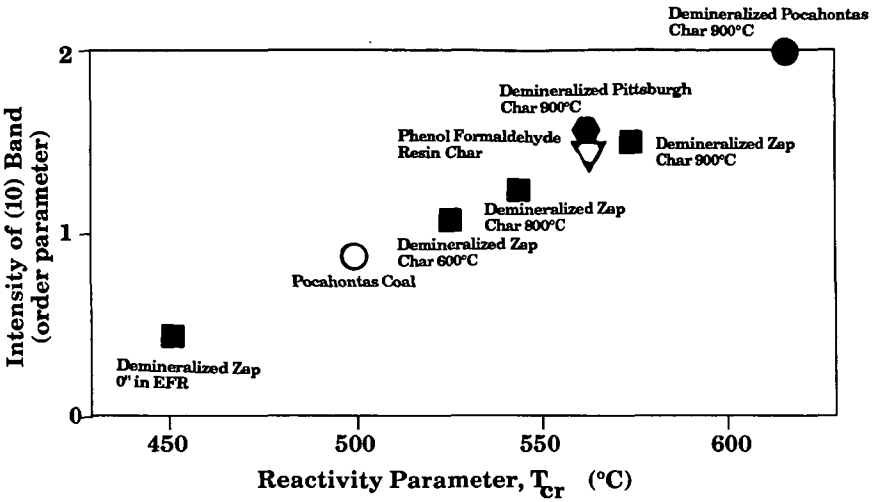

Figure 5. Plot of Order Versus Reactivity for some Eastern and Demineralized Western Chars Formed Under Slow Heating Conditions, and One High Rank Coal.

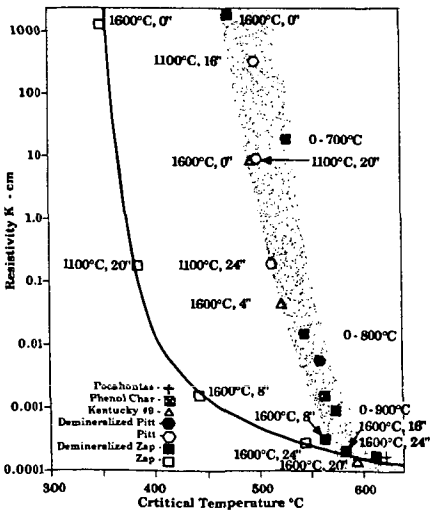

Figure 6. Plot of Resistivity Versus Critical Temperature for a Variety of Chars. The Data for Eastern Coals, or Demineralized Western Coals, Fall Within the Shaded Band.